From ideal gas to relevant three-phase conditions in hydrodenitrogenation reactions and reactors

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Today's modern industrial world depends on hydrocarbon fuels originating from various geographic locations. While alternative energy sources, such as solar, wind and hydropower seem promising, hydrocarbon based fuels still remain the first choice as an energy carriers. Interest in hydrodenitrogenation, has increased recently due to the evermore strict environmental regulations as well as the increasing amounts of nitrogen in the crude oil and its potential presence in oils from a renewable origin. In the present work, pyridine hydrodenitrogenation, see **Figure *1***. is investigated from both an experimental as well as a modelling perspective

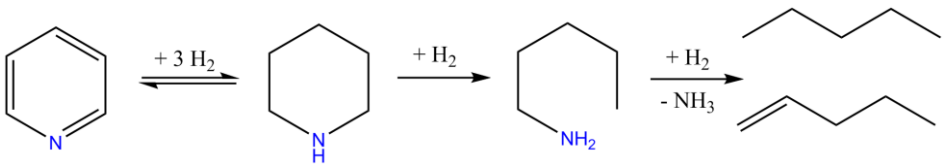

Figure 1. Pyridine hydrodenitrogenation network as observed at gas phase conditions over an industrial NiMo/γ-Al_2O_3 catalyst.

Experimental data obtained at gas phase conditions constitute the basis of our modelling work. In order to develop an adequate kinetic model, experimental data free from any form of hydrodynamic, thermal and transport effects are preferred, if not necessary, *i.e.*, so-called intrinsic kinetics data. Gas phase experimentation is often more straightforward compared to liquid phase experimentation since the stabilisation time is fast and the analysis of a single effluent stream allows more accurate response measurement. The industrial process implementation being operated at three-phase conditions, experimental data acquired at 'liquid phase' conditions are generally considered more relevant for hydrotreating, since realistic feedstocks and industrially relevant conditions can be maintained during the experimental programmes. Studying a single reaction at gas as well as at liquid phase conditions allows a thorough assessment of these phase effects. Starting from a kinetic model constructed based on gas phase data, the extension to liquid phase reactions is achieved by considering the non-idealities induced by the presence of the liquid phase[1,2]. Selection of a model compound such as pyridine allows an in-depth understanding of the hydrodenitrogenation reactions since most of the important reactions occurring within the hydrodenitrogenation can be observed. Reactors used in studying hydrotreating reactions at the gas and the liquid phase have been the of interest for the last few years.

[1] Thybaut, J.W., C.S. Laxmi Narasimhan, and G.B. Marin, **Catalysis Today**, 2006. 111(1-2): p. 94-102.
[2] Raghuveer, C.S., J.W. Thybaut, R. De Bruycker, K. Metaxas, T. Bera, and G.B. Marin, **Fuel**, 2014. 125(0): p. 206-218.

Continuous, Stirred Tank Reactors such as the Berty reactor have been used for studying various reactions at gas phase reactions while the Robinson-Mahoney[3] reactor has been used to perform reactions at three phase conditions. The hydrodynamics in the latter, particularly at industrially relevant conditions, are a matter of deabte. The liquid hold-up, ϵ_L, and volumetric gas-liquid mass transfer coefficient, k_La, which are important parameters in the framework of reactor design and process intensification are estimated based on experiments performed with the so-called dynamic gas absorption technique and step and pulse response of a tracer. While ϵ_L provides insight in the actual phase distribution within the reactor, k_La gives an indication of the extent of mass transfer between the gas and the liquid phase.

[3] Mahoney, J.A., K.K. Robinson, and E.C. Myers, **Chemtech**, 1978. 8(12): p. 758-763.